Chemical Bonding (Part I)

Do the topics appropriate for your lecture
Prepared by Dr. Tony Jacob

https://clc.chem.wisc.edu (Resources page)

Nuggets: Lewis Dot Structures; Resonance; Bond Order; Bond Enthalpy; Formal Charge

LEWIS DOT STRUCTURES: Use valence e\(^{-}\) to create covalent bonding pictures

1. Count valence e\(^{-}\) in molecule. [valence e\(^{-}\): Add valence e\(^{-}\) from each atom, only s and p e\(^{-}\) past the last noble gas (no d electrons)]
2. Draw a skeleton structure. Keep symmetric if possible. Usually (not always) the central atom in the Lewis dot structure is the first atom in the chemical formula.
3. Build octets (8 e\(^{-}\)) around each atom except H (2 e\(^{-}\) around H).
4. Count \#e\(^{-}\) drawn. If it equals the \#valence e\(^{-}\) in Step 1, you're done.
5. If \#e\(^{-}\) is too large: Go to Step 2 and re-draw the skeleton structure, add 1 double bond, and continue with the steps. If \#e\(^{-}\) is still too large, repeat by adding another double bond or create a triple bond.

If \#e\(^{-}\) is too small: Add e\(^{-}\) pairs to the central atom.

Other info: F, Cl, Br, and I can have only 1 bond unless they're the central atom. H always has only 1 bond.

LEWIS DOT STRUCTURES: Categories of compounds to draw LDS for (see the next page for examples):

1. "Normal" compounds: follows the octet rule; e.g., NCl\(_3\)
2. Charged species: add charge to \#valence e\(^{-}\) for anions, e.g., for SO\(_4\)^{2-} add 2 to valence e\(^{-}\) count
   \((1(6) + 4(6) + 2 = 32e^{-})\); subtract charge from \#valence e\(^{-}\) for cations, e.g., NH\(_4\)^{+} \((1(5) + 4(1) - 1 = 8e^{-})\)
3. Multiple bonds: double or triple bonds; e.g., O\(_2\), N\(_2\), etc.
4. Resonance structures: typically, a double bond that moves to an equivalent location, e.g., CO\(_3\)^{2-}, C\(_6\)H\(_6\)
5. Central atom with more than 8e\(^{-}\): central atom must be in the 3rd period or later of Periodic Table, e.g., SF\(_6\)
6. Central atom with less than 8e\(^{-}\): B and Be compounds commonly; e.g., BF\(_3\); in this example B has 6e\(^{-}\); B and Be can have 8e\(^{-}\), e.g., BF\(_4\)^{-}
7. Oxyacids = H\(_n\)XO\(_m\): skeleton structure: X in middle; H’s bonded to O’s, e.g., H\(_2\)SO\(_4\), HNO\(_3\)
8. Individual atoms
9. Organic molecules (e.g., CH\(_4\), C\(_2\)H\(_2\), C\(_2\)H\(_4\), C\(_2\)H\(_6\), C\(_3\)H\(_8\), CH\(_3\)COOH; H\(_2\)CO; NH\(_2\)(CO)NH\(_2\), etc.);
   (connect C atoms together and make sure the \#bonds is correct: C has 4 bonds; N has 3 bonds usually; O has 2 bonds usually; H = 1 bond)
10. Radicals: have an odd \#e\(^{-}\), e.g., NO \((1(5) + 1(6) = 11e^{-})\)
11. Ionic compounds (if covered): e.g., NaCl = [Na]^+ [:\text{Cl}:-]
<table>
<thead>
<tr>
<th>Category</th>
<th>Step 1: count valence electrons</th>
<th>Step 2: draw skeleton structure</th>
<th>Step 3: build octets</th>
<th>Step 4: check LDS for #e⁻</th>
<th>ANSWERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NCl₃ (“simple”)</td>
<td>1(N) + 3(Cl) = 1(5) + 3(7) = 26e⁻</td>
<td><img src="image" alt="Cl-N-Cl" /></td>
<td><img src="image" alt="Cl:N-Cl:" /></td>
<td>26e⁻ → done! ✓</td>
<td><img src="image" alt="Cl-N-Cl:" /></td>
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<tr>
<td>2. SO₄²⁻ (charged)</td>
<td>1(S) + 4(O) + 2 = 1(6) + 4(6) + 2 = 32e⁻</td>
<td><img src="image" alt="O-S-O" /></td>
<td><img src="image" alt="O:S-O:" /></td>
<td>32e⁻ → done! ✓</td>
<td><img src="image" alt="O:S-O:" /></td>
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<tr>
<td>3. N₂ (multiple bond)</td>
<td>2(N) = 2(5) = 10e⁻</td>
<td><img src="image" alt="N=N" /></td>
<td><img src="image" alt="N=N" /></td>
<td>14e⁻ → too many e⁻ add a multiple bond</td>
<td><img src="image" alt="N=N" /></td>
</tr>
<tr>
<td>4. O₃ (resonance)</td>
<td>3(O) = 3(6) = 18e⁻</td>
<td><img src="image" alt="O=O=O" /></td>
<td><img src="image" alt="O=O=O" /></td>
<td>18e⁻ → done! ✓ resonance → place double bond in second location</td>
<td><img src="image" alt="O=O=O" /></td>
</tr>
<tr>
<td>5. BCl₃ (less than an octet)</td>
<td>1(B) + 3(Cl) = 1(3) + 3(7) = 24e⁻</td>
<td><img src="image" alt="Cl-B-Cl" /></td>
<td><img src="image" alt="Cl:B-Cl:" /></td>
<td>26e⁻ → too many e⁻ add a multiple bond</td>
<td><img src="image" alt="Cl:B-Cl:" /></td>
</tr>
<tr>
<td>6. SF₄ (more than an octet)</td>
<td>1(S) + 4(F) = 1(6) + 4(7) = 34e⁻</td>
<td><img src="image" alt="F-S-F" /></td>
<td><img src="image" alt="F:S:F" /></td>
<td>32e⁻ → too few e⁻ add e⁻ pairs to central atom → 34e⁻ → done! ✓</td>
<td><img src="image" alt="F:S:F" /></td>
</tr>
<tr>
<td>7. H₃PO₄ (oxyacid)</td>
<td>1(P) + 4(O) + 3(H) = 1(5) + 4(6) + 3(1) = 32e⁻</td>
<td><img src="image" alt="H-O-P-O-H" /></td>
<td><img src="image" alt="H=O=O=O" /></td>
<td>32e⁻ → done! ✓</td>
<td><img src="image" alt="H=O=O=O" /></td>
</tr>
<tr>
<td>8. N (atom)</td>
<td>1(N) = 1(5) = 5e⁻</td>
<td><img src="image" alt="N" /></td>
<td><img src="image" alt="N" /></td>
<td>5e⁻ → done! ✓</td>
<td><img src="image" alt="N" /></td>
</tr>
<tr>
<td>9. NaCl (ionic)</td>
<td>1(Na) + 1(Cl) = 1(1) + 1(7) = 8e⁻</td>
<td><img src="image" alt="Na-Cl" /></td>
<td><img src="image" alt="Na-Cl" /></td>
<td>8e⁻ → done! ✓ ionic compound charged and needs brackets; both Na and Cl have octets; Na has a [Ne] octet w/o e⁻ shown</td>
<td><img src="image" alt="Na-Cl" /></td>
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<tr>
<td>10. NO (odd #e⁻ = radical)</td>
<td>1(N) + 1(O) = 1(5) + 1(6) = 11e⁻</td>
<td><img src="image" alt="N-O" /></td>
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<td>14e⁻ → too many e⁻ add a multiple bond</td>
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Assign FC → structure with 1e⁻ on N is better; O is more EN than N → structure with 1e⁻ on N is again better; both structures probably exist but structure with 1e⁻ on N is “better” based on FC and EN. Better LDS: N=O.
**RESONANCE:** Multiple bonds can sometimes be placed in several equivalent locations. If this occurs, you **must draw all structures** (called resonance structures) for the complete and correct LDS (e.g., all two LDS for ozone, O₃, all three LDS for carbonate, CO₃²⁻, and all two LDS for benzene, C₆H₆ must be drawn to be correct).

![Resonance Structures Diagram]

**BOND ORDER (BO)**

- Single bond = sharing of 1 e⁻ pair; BO = 1
- Double bond = sharing of 2 e⁻ pairs; BO = 2
- Triple bond = sharing of 3 e⁻ pairs; BO = 3
- Multiple Bonds = Double or Triple bonds.

With resonance structures (one of several methods):  
**Bond Order** =  
\[
\text{# bonds} \over \text{# locations bonds are distributed}
\]

**BO↑** or **Atomic Radii↓** ⇒ bond strength↑ bond length↓ bond dissociation energy↑

**BOND ENTHALPIES (D):** The energy needed to break or make a bond; break bonds: endothermic; form bonds: exothermic; can be used to estimate ΔH_rxn (more accurate if chemicals are in the gas phase)

\[
\Delta_r H = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}
\]

**Example 4:** What is the enthalpy of reaction of CH₄(g) combusting?

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)
\]

**Answer 4:**

**Step 1:** Draw LDS of each molecule to determine whether bonds are single, double, etc.

![LDS Diagram]

**Step 2:** Determine bonds broken (reactants) and formed (products); keep in mind stoichiometric coefficients

- **Bonds broken:** 4 C–H bonds; 2 O=O bonds (each O₂ molecule has 1 O=O bond and there are 2 O₂ molecules so there are 2 O=O bonds)
- **Bonds formed:** 2 C=O bonds; 4 O–H bonds (each H₂O has 2 O–H bonds and there are 2 H₂O molecules so there are 4 O–H bonds)

**Step 3:** Calculate ΔH_rxn

\[
\Delta H_{\text{rxn}} = [4(D_{\text{C-H}}) + 2(D_{\text{O=O}})] - [2(D_{\text{C=O}}) + 4(D_{\text{O-H}})]
\]

the needed bond enthalpy values (D) would be provided for the next step

\[
\Delta H_{\text{rxn}} = [4(416) + 2(498)] - [(2(803) + 4(467))] = -814\text{kJ/mol}
\]
FORMAL CHARGE (FC): The "charge" on an atom as determined from the LDS with bonded e⁻ shared equally

Formula: \[ \text{Formal Charge} = \#\text{valence e}^- - (\#e^- \text{ around atom shown in LDS}) \]

\[ \sum \text{Formal Charges} = \text{Total Charge on Molecule} \]

Example 2: Assign formal charges to each atom in NCO⁻ (use this LDS): \[ \text{N} \overset{\cdots}{\text{C}} \overset{\cdots}{\text{O}} \]

Answer 2:

\[ \text{FC} = \#\text{valence e}^- - \#e^- \text{(LDS)} \]

Replace bonds with e⁻ to see #e⁻ around atom in LDS; e⁻ in bonds are split between adjoining atoms; lone pairs of e⁻ stay with atom

N: 5 valence e⁻ N: 6 e⁻ in LDS
C: 4 valence e⁻ C: 4 e⁻ in LDS
O: 6 valence e⁻ O: 6 e⁻ in LDS

Lewis dot resonance structure that contributes the most based on better Formal Charges (skip if not covered!)

1. Has the smaller (preferably zeros) formal charges.
2. Has more zeros for formal charges.
3. If there is a choice between 2 structure with same set of formal charges and same number of zeros, the more prevalent structure has the more negative formal charges on the more electronegative atom.

Example 3: Of the four ClO₃⁻ structures shown below which contributes the most based on formal charges? EN(Cl) = 2.7; EN(O) = 3.4

Answer 3: Step 1: Assign FC to all atoms in all structures.

Cl: 7 – 5 = +2
O (single bond): 6 – 7 = -1

Cl: 7 – 6 = +1
O (single bond): 6 – 7 = -1
O (double bond): 6 – 6 = 0

Cl: 7 – 7 = 0
O (single bond): 6 – 7 = -1
O (double bond): 6 – 6 = 0

Cl: 7 – 8 = -1
O (single bond): 6 – 7 = -1
O (double bond): 6 – 6 = 0

Step 2: Eliminate structures based on Rule 1, then Rule 2, then Rule 3 above to find the structure that contributes the most based on better formal charges.

1. Eliminate Structure I because of the larger FC on the Cl (Rule 1: smaller FC are better). This is the only structure with a +2 FC.

2. Eliminate Structure II because it only has 1 zero FC while Structures III and IV each have 3 zeros for FC (Rule 2: more zeros are better).

3. Eliminate Structure IV because the more EN atom, O (EN(Cl) = 2.7 versus EN(O) = 3.4), should have the more negative FC (Rule 3). Structure III: FC(Cl) = 0 and FC(O) = -1; Structure IV: FC(Cl) = -1 and FC(O) = 0.

4. Better structure based on FC. Rule 1: smaller FC better. Rule 2: more zeros for FC are better. Rule 3: the more EN atom gets the more negative FC. Structure III contributes more based on FC even though it violates the octet rule.

ClO₃⁻ Structures:

I
\[ \overset{(-1)}{\text{O}} \overset{(-1)}{\text{Cl}} \overset{(-1)}{\text{O}} \]

II
\[ \overset{(0)}{\text{O}} \overset{(+1)}{\text{Cl}} \overset{(-1)}{\text{O}} \]

III
\[ \overset{(0)}{\text{O}} \overset{(+1)}{\text{Cl}} \overset{(-1)}{\text{O}} \]

IV
\[ \overset{(0)}{\text{O}} \overset{(+1)}{\text{Cl}} \overset{(-1)}{\text{O}} \]
1. **Practice drawing Lewis dot structures.** Draw the Lewis dot structures for the following molecules.

   a. NF₃  b. SeF₂  c. BF₄⁻  d. NH₄⁺  e. PO₃³⁻  f. Cl₂  g. SO₄²⁻  h. HCN  i. N₂  j. CH₂Cl₂
   k. ClO₄⁻  l. COCl₂  m. SO₂  n. CO₃²⁻  o. NO₃⁻  p. B  q. O  r. BF₃  s. BeF₂  t. OH (not OH⁺)
   u. IF₄⁻  v. KrF₄⁺²  w. IBr₃  x. HNO₂

2. Draw the Lewis dot structures for the following organic molecules.

   a. CH₃CH₃  b. C₂H₄  c. CH₃CH₂OH  d. CH₃CH₂OCH₂CH₃  e. C₂H₂

3. Which of the following chemicals does not obey the octet rule?

   a. CH₄  b. SiH₄  c. SeF₄  d. BH₄⁻  e. IF₄⁺³

4. Which of the following molecules will have resonance structures?

   I. N₂  II. CO₃²⁻  III. NO₃⁻  IV. BrF₃

   a. II  b. II and III  c. II, III, and IV  d. I  e. IV

5. Consider the following covalent single bonded pairs of atoms; which bond will be shortest?

   a. N–F  b. P–Cl  c. N–Cl  d. P–F  e. all will be the same

6. I. What is the formal charge on the S in SO₃²⁻?

   a. -2  b. -1  c. 0  d. 1  e. 2

II. What is the formal charge on the N in NO₂⁻?

   a. -2  b. -1  c. 0  d. 1  e. 2

7. Which molecule has the strongest carbon oxygen bond?

   a. CO₃²⁻  b. CO  c. CO₂  d. H₂CO (C is central atom)  e. They are all the same strength.

8. Consider the bond lengths below. A reasonable average C–O bond length in CO₃²⁻ would be:

   C–O single bond: 1.43 Å  C=O double bond: 1.23 Å  C≡O triple bond: 1.09 Å

   a. 1.43 Å  b. 1.36 Å  c. 1.23 Å  d. 1.15 Å  e. 1.09 Å

9. I. Consider the following list of compounds. Rank the molecules from smallest to largest N–O bond length.

   NO₂⁻  NO₃⁻  NO⁺  NO⁻

   a. NO⁺ < NO⁻ < NO₂⁻ < NO₃⁻  b. NO₃⁻ < NO₂⁻ < NO⁻ < NO⁺  c. NO₃⁻ < NO⁺ < NO₂⁻ < NO⁻

II. Using the same compounds above, which compound will have the greatest N–O bond enthalpy?

10. Based on Lewis dot structures, which molecule could not exist? If all can exist, select choice “e”.

    a. PBr₅  b. N₂H₂  c. PCl₃  d. NF₅  e. all can exist
11. What is the change in enthalpy for the reaction (ΔH_{\text{rxn}}) using the bond enthalpies listed below? (Hint: Draw the Lewis dot structures for each chemical in the reaction.)

\[ \text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{–CH}_2\text{–OH}(\text{g}) \]

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<td>C–H</td>
<td>416</td>
<td>C–O</td>
<td>695</td>
</tr>
<tr>
<td>C–O</td>
<td>336</td>
<td>O–H</td>
<td>467</td>
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</table>

12. What is the chlorine–chlorine (Cl–Cl) bond enthalpy given the bond enthalpies and ΔH_{\text{rxn}} listed below? (Hint: Draw the Lewis dot structures for each chemical in the reaction.)

\[ \text{H}_2\text{CO}(\text{g}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{Cl}_2\text{CO}(\text{g}) + 2\text{HCl}(\text{g}) \quad \Delta H_{\text{rxn}} = -200\text{kJ} \]

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<td>327</td>
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\[ \text{a. 484kJ} \quad \text{b. 242kJ} \quad \text{c. 26.5kJ} \quad \text{d. 53.0kJ} \quad \text{e. -208kJ} \]

13. What is the carbon–chlorine (C–Cl) bond enthalpy in CHCl\textsubscript{2}–CHCl\textsubscript{2} given the bond enthalpies and ΔH_{\text{rxn}} listed below? (Hint: Draw the Lewis dot structures for each chemical in the reaction; note that the C atoms are bonded together in the product molecule.)

\[ \text{C}_2\text{H}_2 + 2\text{Cl}_2 \rightarrow \text{CHCl}_2–\text{CHCl}_2 \quad \Delta H_{\text{rxn}} = -367\text{kJ} \]

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\[ \text{a. 484kJ} \quad \text{b. 242kJ} \quad \text{c. 26.5kJ} \quad \text{d. 53.0kJ} \quad \text{e. -208kJ} \]

(\text{The next two questions involve choosing the more dominant resonant structure based on formal charge; skip if not covered!})

14. Given the 3 resonance drawings of N\textsubscript{2}O, which structure would contribute the most based on better formal charges?

\[ \text{I. } \overset{\text{N}}{\text{N}}=\overset{\text{O}}{\text{O}} \quad \text{II. } \overset{\text{N}}{\text{N}} \equiv \overset{\text{O}}{\text{O}} \quad \text{III. } \overset{\text{N}}{\text{N}} \equiv \overset{\text{N}}{\text{O}} \]

\[ \text{a. I} \quad \text{b. II} \quad \text{c. III} \quad \text{d. I and III} \quad \text{e. All equally important.} \]

15. Shown below are four possible Lewis dot structures for SO\textsubscript{3}\textsuperscript{2} without any resonance structures drawn. Which structure contributes the most based on preferred formal charges? Explain your answer.

\[ \text{I. } \overset{\text{O}}{\text{O}} \quad \text{II. } \overset{\text{O}}{\text{O}} \quad \text{III. } \overset{\text{O}}{\text{O}} \quad \text{IV. } \overset{\text{O}}{\text{O}} \]

\[ \text{I. } \overset{\text{O}}{\text{O}} \quad \text{II. } \overset{\text{O}}{\text{O}} \quad \text{III. } \overset{\text{O}}{\text{O}} \quad \text{IV. } \overset{\text{O}}{\text{O}} \]
ANSWERS

1. a. \( \text{H}_2\text{O}_2 \) b. \( \text{Se}_2\text{F}_4 \) c. \( [\text{F}:-\text{B}::\text{F}]^- \) d. \( [\text{H}:-\text{N}::\text{H}]^+ \) e. \( [\text{P}::\text{O}::\text{O}]^- \)
   f. \( [\text{O}::\text{O}::\text{O}]^- \) g. \( [\text{Cl}:-\text{Cl}::\text{Cl}]^- \) h. \( \text{H}-\text{C}:=\text{N} \) i. \( \text{iN}:=\text{N} \) j. \( \text{F} \)
   k. \( [\text{O}::\text{O}::\text{O}]^- \) l. \( [\text{Cl}:-\text{C}::\text{Cl}]^- \) m. \( \text{O}::\text{S}::\text{O} \rightarrow \text{O}::\text{S}::\text{O} \)
   n. \( [\text{O}::\text{O}::\text{O}]^- \) o. \( [\text{O}::\text{O}::\text{O}]^- \) p. \( \text{B} \)
   q. \( \text{O} \) r. \( [\text{F}:-\text{B}::\text{F}]^- \) s. \( [\text{F}:-\text{Be}::\text{F}]^- \) t. \( \text{radical} \)
   u. \( [\text{F}::\text{F}::\text{F}]^- \)
   v. \( [\text{F}::\text{F}::\text{F}]^- \) w. \( \text{Br} \) x. \( \text{H}-\text{O}::\text{N}::\text{O} \)

2. a. \( \text{H}::\text{H}::\text{C}::\text{O} \) b. \( \text{H}::\text{C}::\text{C}::\text{H} \) c. \( \text{H}::\text{C}::\text{C}::\text{O} \) d. \( \text{H}::\text{C}::\text{C}::\text{H} \) l. \( \text{H}::\text{C}::\text{C}::\text{H} \)

3. c \{ \( \text{H}::\text{H}::\text{F} \) \( [\text{H}-\text{C}::\text{H}]^- \) \( [\text{F}:-\text{B}::\text{F}]^- \) \}

4. b \{ \( \text{N}_2::\text{iN}::\text{N}::\text{N} \) \( \text{CO}_3^{2-} \) \( [\text{O}::\text{O}::\text{O}]^- \) \( \text{NO}_3^- \) \( \text{BrF}_3 \) \}

5. d \{ \( \text{H}_2\text{O}_2 \) \( \text{H}_2\text{O}_2 \) \( \text{H}_2\text{O}_2 \) \( \text{H}_2\text{O}_2 \) \}
5. a  {this is an atomic size question; smaller atoms → closer together and will have a smaller bond
length and stronger bond energy; between P–Cl and N–Cl: N–Cl has a smaller bond length;
between N–F and P–F: N–F has a smaller bond length; between N–F and N–Cl: N–F has a small
bond length}

![atomic radii increasing](image)

6. I. d  {Draw Lewis dot structure; S: 6 - 5 = 1
II. c  {Draw Lewis dot structure; N: 5 - 5 = 0

7. b  {“a”: \[ \begin{array}{cc}
    & \ddots \\
    \vdots & \ddots \\
    \vdots & \vdots \\
\end{array} \]

    \text{BOC-O} = 1.33; “b”: \( \text{BO} \equiv \ddots \text{BO} \); \( \text{BOC-O} = 3; \)

    “c”: \( \text{BO} \equiv \ddots \text{BO} \); \( \text{BOC-O} = 2; “d”\):

8. b  {From the Lewis dot structure, including the resonance structures, the C−O bond is between a single and double bond with
BO = \( \frac{4}{3} \) bonds. Hence, the bond length is between 1.43Å (single bond) and 1.23Å (double bond).

9. I. a.  {Longest bond has smallest bond order; NO\(^+\): \( \text{\ddots N} \equiv \ddots \text{O} ^+ \) has N-O triple bond with BO = 3;

    NO\(^-\): \( \text{\ddots N} \equiv \ddots \text{O} ^- \) has N-O double bond with BO = 2; NO\(_2\)^-: \( \text{\ddots N} \equiv \ddots \text{O} ^- \) has N-O with BO = \( \frac{3}{2}; \)

    NO\(_3\)^-: \( \text{\ddots N} \equiv \ddots \text{O} ^- \) has N-O with BO = \( \frac{4}{3}; \) NO\(_3\)^+: has smallest BO → longest bond length}

II. NO\(^+\)  {Greater BO → greater bond enthalpy; NO\(^+\) has N-O triple bond → greatest BO (BO = 3) → greatest bond enthalpy}

10. d  {PBr\(_5\): \( \text{\ddots P} \equiv \ddots \text{Br} \); N\(_2\)H\(_2\): \( \text{N} \equiv \text{N} \equiv \ddots \text{H}\); PCl\(_3\): \( \text{Cl} \equiv \text{Cl} \); NF\(_5\): \( \text{\ddots N} \equiv \ddots \text{F} \) you need to put 10 electrons around N;

    this is only allowed for elements in the 3rd period or later; N is in the 2nd period}

11. -43kJ  {Draw Lewis dot structures of all chemicals:

    \[ \Delta H_{\text{rxn}} = \Sigma \text{D bonds broken} - \Sigma \text{D bonds formed} = [1(\text{C-C}) + 4(\text{C-H}) + 2(\text{O-H})] - [1(\text{C-C}) + 5(\text{C-H}) + 1(\text{C-O}) + 1(\text{O-H})] = [1(598) + 4(416) + 2(467)] - [1(356) + 5(416) + 1(336) + 1(467)] = -43kJ]
12. b  {Draw Lewis dot structures of all chemicals:}

\[
\begin{array}{ccc}
\text{H} & \text{C} & \text{H} \\
\text{H} & \text{O} & \text{Cl} \\
\text{Cl} & \text{Cl} & \text{H} \\
\end{array}
\]

\[
\begin{array}{ccc}
\text{H} & \text{C} & \text{Cl} \\
\text{Cl} & \text{Cl} & \text{H} \\
\end{array}
\]

\[
\Delta H_{\text{rxn}} = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}} \text{ to calculate the value of the Cl–Cl bond.}
\]

\[
\Delta H_{\text{rxn}} = [2(\text{C–H}) + 1(\text{C=O}) + 2(\text{Cl–Cl})] - [(2(\text{C–Cl}) + 1(\text{C=O}) + 2(\text{H–Cl})];
\]

\[
-200 = [2(416) + 1(695) + 2(x)] - [(2(327) + 1(695) + 2(431)); x = 242]
\]

13. 327kJ/mol  \{\Delta_f H = [2(\text{C–H}) + 1(\text{C=C}) + 2(\text{Cl–Cl})] - [(2(\text{C–H}) + 4(\text{C–Cl}) + 1(\text{C–C})];
\]

\[
-367 = [2(416) + 1(813) + 2(242)] - [(2(416) + 4(x) + 1(356)]; -367 = 2129 - [1188 +4x]; -367 = 941 - 4x; 4x = 1308;
\]

\[
x = 327kJ/mol
\]

14. c  \{eliminate the second diagram because of the larger FC, -2:
\]

\[
\text{between the first and third structures, since O is more EN than N, the O atom should have the more negative FC, hence, eliminate the first structure:}
\]

\[
\text{the third structures contribute the most because it has the better FC:}
\]

15. Structure II contributes the most based on formal charges.  \{Structure IV contributes the least because of the high FC. Structure I also will not contribute much because it has fewer zeros than Structures II or III. The difference between Structures II and III is a -1 FC on the O atom and a FC of 0 on the S (Structure II) and the reverse of that for Structure III. Since O is more electronegative than S the O atom should have the more negative FC. Therefore, Structure II contributes the most based on formal charges.
\]

\[
\begin{bmatrix}
\text{I} & \text{II} & \text{III} & \text{IV}
\end{bmatrix}
\]

\[
\text{I: } \begin{cases}
\text{Cl} & \text{O} & \text{H} \\
\text{O} & \text{C} & \text{Cl} \\
\text{H} & \text{Cl} & \text{Cl}
\end{cases}
\]

\[
\text{II: } \begin{cases}
\text{H} & \text{Cl} & \text{Cl} \\
\text{Cl} & \text{C} & \text{O} \\
\text{H} & \text{Cl} & \text{Cl}
\end{cases}
\]

\[
\text{III: } \begin{cases}
\text{H} & \text{Cl} & \text{Cl} \\
\text{Cl} & \text{C} & \text{O} \\
\text{H} & \text{Cl} & \text{Cl}
\end{cases}
\]

\[
\text{IV: } \begin{cases}
\text{H} & \text{Cl} & \text{Cl} \\
\text{Cl} & \text{C} & \text{O} \\
\text{H} & \text{Cl} & \text{Cl}
\end{cases}
\]